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An Evaluation of Three Empirical Air-to-Leaf Models for Dioxin-Like Compounds

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Introduction

Three empirical air-to-leaf models for estimating grass concentrations from air concentrations are described and tested against a field data set. All are empirical in that they are founded on simplistic bioconcentration and related approaches which rely on field data for their parameterization. The three models are applied to field data originating from the United Kingdom in which air and field grass concentrations, and dioxin depositions, were measured for a concurrent sampling period. This modeling exercise is published in expanded form in Lorber Pinsky¹. Details of the models and the exercises can be found there.

Field Site Data

Jones and Duarte-Davidson² present the results of an extensive monitoring study of dioxin concentrations in air and grass, as well as deposition fluxes, from three sites over three time periods between 1992 and 1993 in the United Kingdom. The three sites include a rural background site, an urban site, and an industrial site. Two subsets of this data, which are appropriate for air-to-plant model validation purposes, were presented by Jones and Duarte-Davidson². Specifically, this includes concurrently measured concentrations of dioxin and furan congeners, and homologue groups, for air and grass sampled for two of the sites, the industrial and rural background site, for one of the sampling periods, Sep. 14 - Oct. 30, 1993. They also presented the results of their deposition collection for those two sites/sampling periods. We used both sites in model testing¹; only the rural site model evaluations are presented here. Air samples were taken using standard General Works high-volume samplers which took weekly samples of 300-500 m³ air for 4-6 week sampling periods. The glass fiber filters and the polyurethane foam plugs of these samplers (measuring, in theory, the vapor and particle phases, respectively) were collected weekly and composited for each full sampling period to allow for a single measurement of total air concentration of the dioxins, representing around 2000-3000 m³ (depending on the time of the individual sampling periods) of air volume. A bulk deposition sample for each site/sampling period was also collected using "upturned frisbee" collectors. Grass was mowed at

the beginning and end of each sampling period; the second cutting represented the grass yields over the sampling period. Data site used here are shown in Table 1.

Model Overview

The first model was developed for the United States Environmental Protection Agency's (EPA) Reassessment for Dioxin and Related Compounds³. It will be called the EPA model. First, total dioxin concentrations are partitioned into a vapor and a particle phase, using Junge's⁴ model based on aerosol particle densities and the saturated liquid vapor pressure of the semivolatile dioxins. Total plant concentrations are the sum of vapor phase and particle phase impacts. The particle-phase impact model is a simple reservoir mixing model: particle-bound dioxins deposit using a deposition velocity (0.2 cm/sec) to mix in a reservoir of plant matter (the grass yield), and then dissipate (weather) from the plant with a fixed dissipation rate, set equal to a half-life of 14 days in this application. Vapor phase impacts are modeled quite simply using a bioconcentration approach: plant concentration equals air concentration times an "air-to-leaf" bioconcentration factor. This factor was calibrated⁵ based on experimental data on the transfer of dioxins to Welsh Ray Grass⁶. The second model to be evaluated addresses only vapor phase impacts to plants, and will be referred to as the vapor deposition model. It is, in fact, analogous to the EPA model for particle phase impacts to plants; plant concentrations equal a vapor-phase reservoir depositing onto, mixing in, and dissipating from a plant reservoir. This approach has been described and parameterized for vapor phase 2,3,7,8-TCDD impacts to grassy plants by Trapp and Matthies⁷ and Smith et al⁸. Their critical deposition velocity terms were 0.50⁷ and 0.76⁸ cm/sec, and their dissipation rates were 0.374⁷ and 0.159⁸ day⁻¹ (half-lives of 1.8 and 4.4 days). This model is applied to 2,3,7,8-TCDD only using the parameterization of these two authors. McLachlan⁹ developed a simple "scavenging" approach to predict grass concentrations from air concentrations of dioxins. In the scavenging model, McLachlan⁹ assumed that grass scavenges the equivalent of 9 m³ of air per gram of grass, and that corn scavenges 4.5 m³ of air. The important assumption is that plants can scavenge vapors and particles equivalently; therefore, vapor/particle partitioning is unnecessary, and plant concentrations are very simply modeled as the product of total air concentration and the scavenging coefficient, SC. In this application, SC is assigned a value of 9 since the field data is grass.

Procedures and Results of Model Testing

This exercise is a model validation exercise because: 1) all model parameters are assigned values based either on the field data (measured grass yields, e.g.) or values derived from the literature (model parameters such as the SC, e.g.), 2) the key independent variable, in this case air concentrations, are measured and are input into the model, and 3) the key dependent prediction, in this case grass concentrations, are also measured and are to be compared with model predictions. A model validation might be considered successful if the predictions match the observations in a satisfactory manner. Model goodness-of-fit was evaluated using the absolute and signed difference between the natural logs of the measured and modeled grass concentrations. The signed error, or bias, measures the systematic tendency of the model to under or overpredict; a bias near 0 suggests that the model underpredicts and overpredicts by about the same amount. The absolute error calculation describes model variation; how close the model predictions come to the observations, regardless of whether the model over or underpredicted. A value close to 0 suggests a very good match between predictions and observations. Log concentrations were used

because there were a wide range in grass concentrations, from sub-ppt concentrations for the lower chlorinated dioxins to concentrations near 100 ppt for the homologue groups. As noted above, only the rural air and grass data from the UK are used in this application. Of 25 air:grass observed data points (17 dioxin-like congener concentrations and 8 homologue group concentrations), we used 22. In order to obtain independent data points for model validation and goodness-of-fit exercises, we subtracted the congener-specific data from their respective homologue groups. In doing so, it was found that, in three instances (HpCDF, HxCDF, and HpCDF), subtraction of the congener concentrations from the homologue group resulted in negative air concentrations. There was obviously some measurement error in this data set. The air:grass pairs for these three homologue groups were, therefore, not considered further. The remaining 22 data pairs were found to be highly correlated, with a correlation coefficient of 0.92. Generation of dioxin toxic equivalent (TEQ) concentrations were developed using the International Toxicity Equivalency Factors¹⁰.

Figure 1 shows the application of the EPA model and the scavenging model to the rural field site data, with observed grass concentrations on the x-axis and predicted grass concentrations on the y-axis. The dashed line shows where the predicted equals observed would occur. As seen in this figure, the EPA model provided a significantly better fit to the data compared to the scavenging model. The predicted TEQ concentration by the EPA model was 6.6 pg/g dry, compared to the observed concentration of 6.0 pg TEQ/g dry. The bias was 0.012, giving a bias factor of $\exp(0.012) = 1.01$ and suggesting that there appeared to be no particular bias in either under or overpredicting grass concentrations. The absolute error was 0.396, meaning that the predicted grass concentrations tended to be within a factor of about 1.5 ($e^{0.396}$) of measured concentrations. In contrast, the scavenging model predicted a grass concentration about a third as much as observed, at 1.85 pg TEQ/g dry. The absolute error was 1.325, and the bias was its negative counterpart, -1.325. This means that the model underpredicted concentrations in all instances, and that this underprediction was by a factor of 3.8 ($e^{1.325}$).

Whereas the scavenging ratio of 9.0 may have been appropriate for the field data used by McLachlan⁹ in the development of this approach, it is far too low for this particular data set. A calibration exercise was performed on the 22 air/grass data points in the rural site to determine the best-fit value for the scavenging coefficient. In this exercise, the least squares fit of the difference between predicted and measured log grass concentrations was sought. The best fit was found at the constant scavenging coefficient of 36.4, or 4 times the scavenging coefficient suggested by McLachlan⁹. With this value, the goodness-of-fit measures for the scavenging and EPA models were quite comparable: the former had a bias of 0 (by definition of the least squares fit) 0, and an absolute error of 0.417, while the EPA model had a bias of 0.012 and an absolute error of 0.396.

A critical assumption of the scavenging approach is that vapor and particle-phase dioxins are scavenged equivalently from the air. Therefore, a constant scavenging coefficient can be applied to total air concentration to predict total grass concentration. The error terms for the best-fit scavenging ratio suggest this might be reasonable. However, this assumption is not supported by the data in this field site. Figure 2 shows the scavenging ratios calculated for the 22 air:grass data points graphed as a function of the degree of chlorination. For example, there are four data points plotted for degree of chlorination 4 on the x-axis: 2,3,7,8-TCDD, 2,3,7,8-TCDF, the TCDD homologue group, and the TCDF homologue group (note that again the congener concentrations are subtracted from the homologue concentrations for both air and grass in this graph). The scavenging ratios are simply calculated as the grass concentration (in pg/g dry

weight) divided by the air concentration (in pg/m^3). As seen in the figure, there is a clear trend in that the scavenging ratio appears to generally decrease from the tetra to the hepta degrees of chlorination, with perhaps an increase at the octa degree of chlorination. It also suggests more of a trend for the dioxins as compared to the furans.

The experiments on Welsh Ray Grass⁶ used to calibrate the EPA's air-to-leaf transfer factor provided a reason for this trend: when blocking out the particle deposition impacts to potted grass, the authors found that the grass concentrations of the lower chlorinated dioxins and furans were similar to concentrations in potted grass where particle depositions were not blocked out. The authors concluded that the plant concentrations were dominated by vapor-phase dioxins. Since the lower chlorinated congeners exist more in the vapor than in the particle phase, it follows that the lower chlorinated congeners would have a larger overall scavenging coefficient.

Figure 3 shows the comparison of predicted and observed deposition of dioxin; again a dashed line shows the perfect fit between observed and predicted. It is clear that the modeled rates of deposition using the EPA particle-phase model were consistently higher than the measured rates. There was a high degree of correlation between measured and modeled rates, however, with a correlation coefficient of 0.99. The absolute error and bias were 1.12 and 1.06, respectively (for all but one congener/homologue, the model overpredicted deposition), suggesting that the model predictions were, on average, about 3 times higher than observed. This would indicate a systematic bias, either that the model tended to overpredict depositions or that the measurements tended to under-represent depositions to plants (or a combination of both). If the model tended to overpredict deposition, this may have been due to the assumption of a deposition velocity that was too high. Measured deposition velocities can be calculated from the data of Jones and Duarte-Davidson simply as the deposition flux divided by the air concentration (with proper conversions). Average velocities calculated this way were 0.06 cm/sec for the rural site data shown in Figure 3; lower than the 0.20 cm/sec applied in the modeling exercise. Actually, the discrepancy is larger: 0.20 cm/sec was applied to the particle phase concentration, while 0.06 cm/sec was calculated from total air concentrations. Another key modeling parameter that may have caused overestimation in deposition fluxes was the modeled particle phase fraction. As described in EPA³, measured particle phase fractions tend to be significantly lower than modeled fractions. If the smaller measured particle phase fractions were used perhaps with 0.06 cm/sec deposition velocity, than modeled deposition amounts would be similar to measured amounts.

Table 2 shows the comparison of the measured grass concentration of 2,3,7,8-TCDD with the modeled vapor transfer concentration using the EPA vapor transfer model and the two vapor deposition models. It is clear from this table that the vapor deposition algorithm, as parameterized by Smith et al.⁷ and Trapp and Mattheis⁸, predicts concentrations that are over an order of magnitude lower than predictions made by the vapor transfer algorithms of the EPA model, and even lower still than observed grass concentrations. Critical parameters include the deposition velocity and the rate of degradation on the plant. Based on literature¹¹, the deposition velocities set at less than 1.0 cm/sec, were unlikely to be significantly low. The degradation term is more likely inappropriately assigned by these researchers, at least for this field data set. That rate was based on a controlled chamber study, which included an uptake and a degradation phase¹². The degradation phase was conducted in outdoor bright sunlight (personal communication, J. McCrady, US EPA, 1995). Degradation rates derived under these sunlight conditions may not be appropriate for most conditions. A longer half-life would improve model

predictions. However, no data other than McCrady's could be found for the degradation value.

Principal Findings

1. The EPA model which separately modeled the vapor and particle phase impacts provided the best fit of the data to the model; the scavenging model and the vapor deposition models significantly underestimated observed grass concentrations. When the scavenging model was calibrated to the field data, the fit improved significantly.
2. A key premise of the scavenging coefficient model, that vapor and particle phase dioxins equally impact the plants, is not supported by the field data; the lower chlorinated dioxins scavenge more efficiently than the higher chlorinated dioxins.
3. Measured depositions are highly correlated to but systematically lower than modeled depositions, which could be due to modeling assumptions or a systematic measurement bias, or both.
4. The vapor deposition model has two key and uncertain parameters, the deposition velocity and the degradation of vapor-phase dioxins that have deposited on the grass. Of the two, the degradation term is judged to be more uncertain and little data is available to assign values for this parameter for the dioxins.

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Table 1. Observed data for the air-to-plant model validation exercise.*

Compound	Air	Deposition	Grass	Compound	Air	Deposition	Grass
2378-TCDD	0.01	<0.46	0.72	TCDD	0.72	73	66
12378-PCDD	0.03	2.3	1.3	PCDD	PCDD	0.56	54
123478-HxCDD	0.04	2.3	0.93	HxCDD	0.65	38	26
123678-HxCDD	0.08	4.8	2.3	HpCDD	0.71	41	22
123789-HxCDD	0.1	3.8	1.8	OCDD	2.5	166	94
1234678-HpCDD	0.82	41	22	TCDF	1.6	24	93
2378-TCDF	0.33	12	14	PCDF	0.45	18	13
12378-PCDF	0.06	2.5	1.8	HxCDF	0.45	18	13
23478-PCDF	0.1	4.1	2.2	HpCDF	0.22	<1.8	<0.22
123478-HxCDF	0.3	11	5.6	OCDF	0.42	28	13
123678-HxCDF	0.1	4.5	2.2	Units: air - pg/m ³ deposition - pg/m ² -day grass - pg/g. Grass yield = 89 g/m ² dry weight			
123789-HxCDF	0.02	1.8	0.61				
234678-HxCDF	0.14	4.8	2.6				
1234678-HpCDF	0.53	19	12				
1234789-HpCDF	0.11	2.9	1.1				

Figure 1. Comparison of observed and predicted grass concentrations of dioxin and furan congeners for the EPA and the scavenging models. The perfect match of observed and predicted is shown in the dashed observed = predicted line.

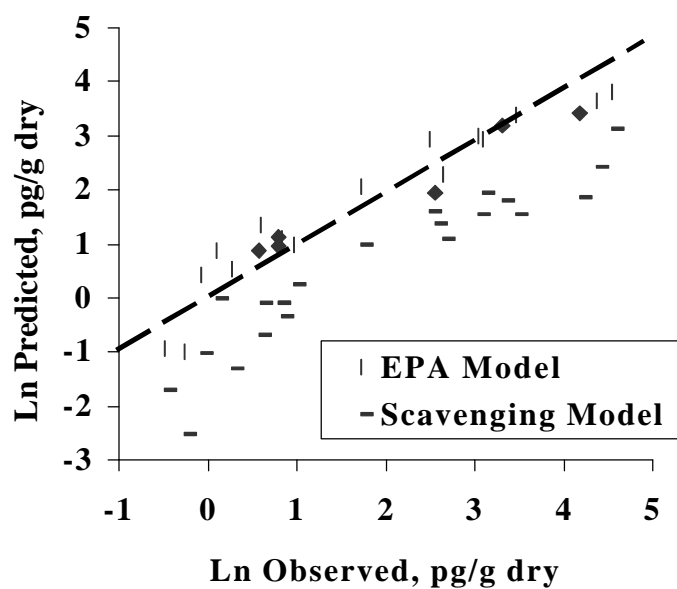


Figure 2. Scavenging coefficient as a function of the degree of chlorination.

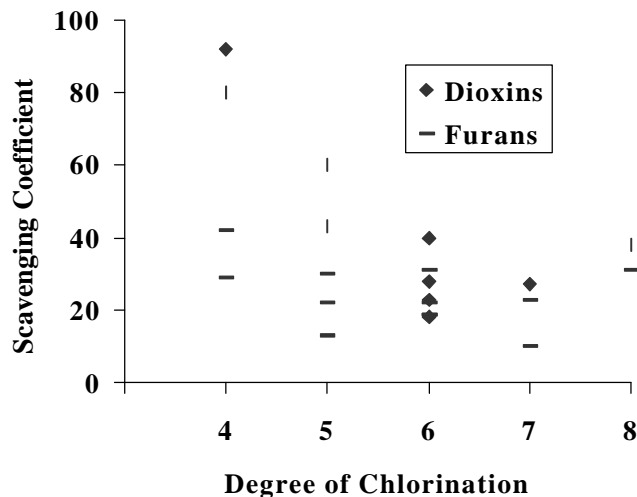


Figure 3. Comparison of observed dioxin/furan deposition and deposition predicted by the EPA model. The perfect match of observed and predicted is shown in the dashed observed = predicted line.

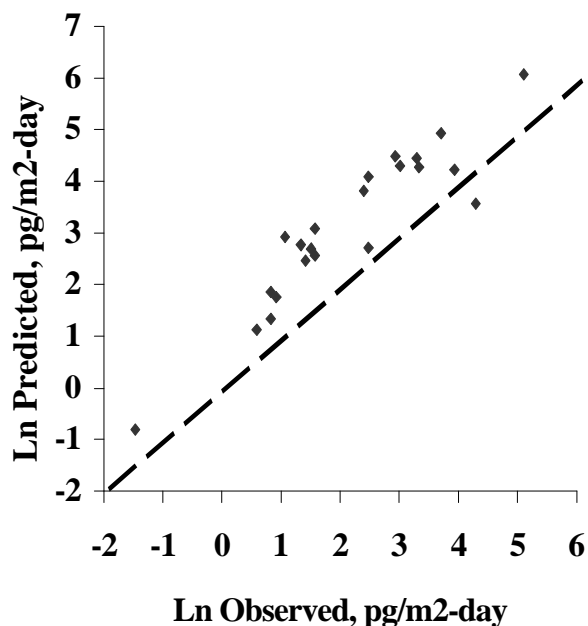


Table 2. Model results comparing the EPA vapor transfer model and the vapor deposition model with the field data for 2,3,7,8-TCDD (concentrations in pg/g dry weight).

Description	2,3,7,8-TCDD grass concentrations, pg/g dry
Observed data	0.76
EPA vapor transfer model ^{3,5}	0.35
Smith et al. model ⁷	0.01
Trapp & Mattheis model ⁸	0.02